

IRREVERSIBLE THERMODYNAMICS AND DERIVATION OF A SYSTEM
OF DIFFERENTIAL EQUATIONS OF MOLECULAR TRANSFER

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IRREVERSIBLE THERMODYNAMICS AND DERIVATION OF A SYSTEM OF DIFFERENTIAL EQUATIONS OF MOLECULAR TRANSFER

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ABSTRACT

Derivation of a system of differential equations of molecular transfer for the case of n interrelated fluxes of generalized charges are presented. The derivation is carried out on the basis of linear laws of irreversible thermodynamics and the law of conservation of matter. Methods of solving boundary-value problems for this system of equations are discussed.

The modern theory of transfer of generalized charges within a capillary-porous medium makes extensive use of the methods of the thermodynamics of irreversible processes. /318*

As is well known, the basis for the thermodynamics of irreversible processes consists of two principles: the linear law and the Onsager reciprocal relation. A great number of irreversible processes are known whose regularities are expressed phenomenologically by the linear relations between cause and effect. According to the linear law, the rate I (result) of approach of a system to a state of equilibrium is proportional to the thermodynamic impetus (force) X (cause), which in turn can be expressed by the potential gradient. For example, the law of heat conductivity concerning the proportionality of the heat flux to the temperature gradient ($I = -\lambda \text{grad } T$), the law of diffusion and the proportionality of a flux of a component of the mixture to the gradient of the concentration ($I_m = -\lambda_m \text{grad } U$), Ohm's law on the proportionality of current density to the potential gradient ($I = -\sigma \text{grad } \phi$), etc.

*Numbers given in margin indicate pagination in original foreign text.

These linear laws served as a basis for deriving the corresponding differential equations (heat conductivity, diffusion, electrical conductivity, etc.).

In contrast to the classical concept, the phenomena of heat transfer, mass of bonded matter, electrical charges, etc., on the basis of which the corresponding differential equations were derived, now are being reconsidered using the thermodynamics of irreversible processes.

Whereas earlier in the study of heat transfer, electricity and mass of bonded matter it was customary to consider independent linear transfer equations, now the initial transfer equations consist of the system of Onsager linear equations, in which any form of transfer is determined by the influence of the direct effect and superposed transfer phenomena. Mathematically the superposition effects are described by additional terms in the expression of the principal transfer law (direct effect). These linear Onsager equations lead to a system of interrelated differential equations of molecular transfer--to a system of differential equations in partial derivatives of the parabolic type relative to the potential fields of distribution of temperature, electricity, mass of bonded matter, etc. /319

According to the linear law, the flux I_i caused by the effect of n generalized forces X_k ($k = 1, 2, \dots, n$), is proportional to these forces

$$I_i = \sum_{k=1}^n L_{ik} X_k \quad (i = 1, 2, \dots, n). \quad (1)$$

The values L_{ik} are called the phenomenological (kinetic) Onsager coefficients. The diagonal coefficients L_{kk} show the intensity of transfer of the k -th generalized charge under the influence of the similar force X_k . The coefficients L_{ik} , when $i \neq k$, are called the drag coefficients and are related to the superposed phenomena.

The Onsager reciprocal relation establishes that with an appropriate selection of the fluxes I_i and X_i the matrix formed from the kinetic coefficients

$$\begin{pmatrix} L_{11} & L_{12} & \dots & L_{1n} \\ L_{21} & L_{22} & \dots & L_{2n} \\ \dots & \dots & \dots & \dots \\ L_{n1} & L_{n2} & \dots & L_{nn} \end{pmatrix} \quad (2)$$

is symmetrical, that is,

$$L_{ik} = L_{ki} \quad (3)$$

This relation is the result of microscopic reversibility.

For example, for the phenomenon of joint occurrence of nonisothermal diffusion and heat conductivity within a porous medium we may write

$$\begin{aligned} I_1 &= L_{11}X_1 + L_{12}X_2, \\ I_2 &= L_{21}X_1 + L_{22}X_2, \end{aligned} \quad (4)$$

where I_1 is the energy flux (heat); I_2 is the flux of the mass of bonded matter. L_{21} and L_{12} establish the relationship between the superposed phenomena (thermal diffusion, that is, the temperature gradient, causes the transfer of matter and diffusive heat conductivity, that is, the gradient of the concentration causes heat transfer). L_{12} is proportional to the Soret coefficient and L_{21} to the Dufeu coefficient.

The equality of the nondiagonal kinetic coefficients $L_{12} = L_{21}$ means there is a symmetry between the influence of the force of diffusion on the heat flux and the influence of the thermal force on the flux of matter. For clarification of the quantitative aspect of the reciprocal influence of different fluxes we will differentiate the linear equations of system (4)

$$\left(\frac{\partial I_1}{\partial X_2} \right)_{X_1} = L_{12}, \quad \left(\frac{\partial I_2}{\partial X_1} \right)_{X_2} = L_{21} \quad (5)$$

On the basis of reciprocal relation (3) we obtain

$$\partial I_1 / \partial X_2 = \partial I_2 / \partial X_1 \quad (6)$$

The increment of the energy flux (heat), related to a ^{unit} increment of the kinetic force X_2 (gradient of the function of distribution of mass of the bonded

matter), is equal to the increment of the flux of matter, related to a unit increment of kinetic force X_1 (temperature gradient).

For derivation of a system of differential equations of molecular transfer we will make some assumptions concerning the model of the thermodynamic system in which the transfer process occurs. We will assume that within an isotropic capillary-porous body (conductor) there are n generalized charges. These generalized charges experience transfer under the influence of n generalized forces X_1, X_2, \dots, X_n , whose potentials are $U_1(x, y, z, t), U_2(x, y, z, t), \dots, U_n(x, y, z, t)$.

Thus, the thermodynamic system is essentially heterogeneous and is assumed to be continuous, that is, any elementary volume of the conductor is filled with all n components of generalized charges.

We will write the generalized forces X_1, X_2, \dots, X_n through the gradients of the corresponding potentials $X_k = -\nabla U_k = -\text{grad} U_k$. Under these conditions the linear equations (1) are written in the form

$$I_k = - (L_{k1} \nabla U_1 + L_{k2} \nabla U_2 + \dots + L_{kn} \nabla U_n) \quad (k = 1, 2, \dots, n). \quad (7)$$

Within the conducting body (conductor) we will consider the elementary volume V , bounded by surface S . We will break down surface S into m arbitrary parts. Assume ΔS_i is the value of the area of the i -th part of surface S ; then

$\Delta E_{ki} = I_k(p'_i, t) \Delta S_i$ is the quantity of the k -th generalized charge, passing

through the surface ΔS_i in a unit time, $(E_k)_m = \sum_{i=1}^m \Delta E_{ki} = \sum_{i=1}^m I_k(p'_i, t) \Delta S_i$

is the approximate value of the total quantity of the generalized charge passing through the entire surface S in a unit time t . Hence

$$E_k = \lim_{m \rightarrow \infty} \sum_{i=1}^m I_k(p'_i, t) \Delta S_i$$

$I_k(p'_i, t) \Delta S_i \rightarrow \iint_S I_k(p', t) dS$ is the quantity of the generalized charge of the k -th flux, passing through control surface S in a unit time. Here the integral applies for the entire surface S of volume V .

In the absence of sources of formation of a k -th generalized charge within volume V , the flux through surface S causes a change of the content of the charge by the value

$$\iiint_V \gamma C_k \frac{\partial U_k}{\partial t} dV.$$

On the basis of the law of conservation of matter the change of the content of the charge in volume V is equal to its loss through surface S, bounding the given volume V, that is,

$$-\int_{(V)} \frac{\partial U_k}{\partial t} \gamma C_k dV = \int_S I_k(p', t) dS. \quad (8)$$

Substituting the value $I_k(p', t)$ using formula (7), we obtain

$$\int_{(V)} \gamma C_k \frac{\partial U_k}{\partial t} dV = \int_S \left[\sum_{i=1}^n L_{ki} \text{grad } U_i \right] dS. \quad (9)$$

Using the M.V. Ostrogradskiy formula, the double integral for surface S is expressed by the triple integral for volume V

$$\int_S \left[\sum_{i=1}^n L_{ki} \text{grad } U_i \right] dS = \int_{(V)} \text{div} \left[\sum_{i=1}^n L_{ki} \text{grad } U_i \right] dV. \quad (10)$$

Equation (9) assumes the form

$$\int_{(V)} \gamma C_k \frac{\partial U_k}{\partial t} dV = \int_{(V)} \text{div} \left[\sum_{i=1}^n L_{ki} \text{grad } U_i \right] dV. \quad (11)$$

Since equation (11) was obtained for any arbitrary volume V, it follows that

$$\gamma C_k \frac{\partial U_k}{\partial t} = \text{div} \left[\sum_{i=1}^n L_{ki} \text{grad } U_i \right] \quad (12)$$

($k = 1, 2, \dots, n$).

System (12) is a system of differential transfer equations in the presence of n interrelated fluxes of generalized charges.

Whereas the thermodynamics of irreversible processes in the investigation of the phenomenon of transfer of heat and matter makes it possible to use their phenomenological laws to take into account some experimentally observed qualitative patterns of behavior and obtain fundamental results from them, analytical solutions of the system disclose the quantitative aspect of transfer.

Thus, the analytical methods of the thermodynamics of irreversible processes, the methods of statistical physics, and mathematical methods for solution of the boundary value problem for system (14) will mutually supplement one another in the general experimental and theoretical investigation of the mechanism of transfer of heat and matter.

A number of new boundary-value problems for the system of differential transfer equations has been solved and published. M. S. Smirnov in references 1 and 2 has presented a method for reducing the boundary-value problem for a system of differential equations of dissipation to the solution of the corresponding boundary-value problem for a differential equation of the heat conductivity equation type. This method considerably simplifies the complex solution of the principal boundary-value problem and gives some new quantitative relations. In particular, in reference 1 a formula (20) is proposed which can be used with simple differentiation for determining the rate of dissipation by the rate of heat transfer.

In references 3 and 4 the author solved some boundary-value problems for system (14) by the method of reducing a system of n differential equations of the parabolic type to nonhomogeneous equations of the heat conductivity type. This method in essence is the generalized Delambre method.

Notations

I_k -- flux of the k -th generalized charge; X -- generalized force; U_k -- scalar potential of the generalized force X_k ; L_{ik} -- Onsager phenomenological coefficients; V -- elementary volume of the conductor; S -- surface of volume V or control surface; p' -- an arbitrary point of surface S ; E -- quantity of the generalized charge; γ -- specific weight of the conductor; C_k -- specific capacitance of the material of the conducting body (conductivity) relative to the k -th generalized charge; a_{kk}^2 -- coefficient of potential conductivity of the k -th generalized charge; ∇ -- the Hamiltonian.

REFERENCES

1. Smirnov, M. S. Inzhenerno-Fizicheskiy Zhurnal, No. 9, 1961.
2. --- Inzhenerno-Fizicheskiy Zhurnal, No. 3, 1962.
3. Tsoy, P. V. DAN (Doklady Akad. Nauk) Tadzhikskoy SSR, No. 2, 1963.
4. --- Inzhenerno-Fizicheskiy Zhurnal, No. 4, 1963.

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